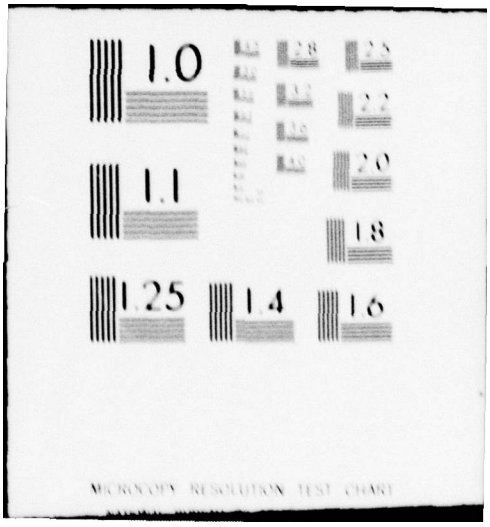
AD-A060 090 TENNESSEE UNIV KNOXVILLE DEPT OF CHEMISTRY F/G 7/4
LOW TEMPERATURE FLUORINATION OF AEROSOL AND CONDENSED PHASE SOL--ETC(U)
SEP 78 J L ADCOCK, E B RENK N00014-77-C-0685
UNCLASSIFIED TR-1 NL

END
DATE FILMED
12-78
DDC


1.0
1.1
1.25
1.4
1.6
2.8
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART

(12) LEVEL II

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0685

Task No. NR 053-669

TECHNICAL REPORT No. 1

Low Temperature Fluorination of Aerosol and Condensed Phase Sol Suspensions of Hydrocarbons Utilizing Elemental Fluorine

by

James L. Adcock and Ehrengard B. Renk
Department of Chemistry
University of Tennessee at Knoxville
Knoxville, Tennessee 37916

Approved for public release; distribution unlimited

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Technical Report No. 1
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): LOW TEMPERATURE FLUORINATION OF AEROSOL AND CONDENSED PHASE SOL SUSPENSIONS OF HYDROCARBONS UTILIZING ELEMENTAL FLUORINE
5. TYPE OF REPORT & PERIOD COVERED: Interim rept.,
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): James L. Adcock and Ehrengard B. Renk
8. CONTRACT OR GRANT NUMBER(s): N00014-77-C-0685

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Department of Chemistry
University of Tennessee- Knoxville
Knoxville, Tn. 37916

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 053-669

11. CONTROLLING OFFICE NAME AND ADDRESS:
Office of Naval Research
Department of Navy
Arlington, VA. 22217

12. REPORT DATE: September 1978
13. NUMBER OF PAGES: 14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release, distribution unlimited.

12 15 p. 14 TR-1

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Aerosol
Fluorination
Elemental Fluorine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report outlines the development of a new method of low temperature fluorination. This method involves the reaction of gaseous elemental fluorine upon a solid-phase particulate aerosol at temperatures below room temperature. The rationale for the development of this method is that it is a flow process but preserves the low temperature, solid phase fluorination features of the low temperature gradient reactor system developed by

346 670

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Adcock, Marashin and Lagow while eliminating the inherent reliance on low temperature mass transport which results in long reaction times and the essentially batch nature of gradient reactor process.

This report discusses developments leading up to the first successful fluorination of a solid-phase particulate aerosol using elemental fluorine.

Introduction

This report outlines the development of a new concept in low temperature fluorination. The method involves the reaction of gaseous elemental fluorine upon a solid-phase, particulate aerosol at temperatures below room temperature. The rationale for the development of this method is that it is a flow process and has extensive flexibility which allows the optimum conditions of flow, temperature and reaction rate to be achieved without undue limitations arising from the physical state or volatility of the starting material. Practically any material which may be converted into a solid-phase porticulate aerosol may be fluorinated by this method. Another potential advantage is that the stoichiometry of the reaction is easily controlled by simply varying the molar ratios of hydrocarbon to fluorine. This may be of major importance in studies designed to achieve selectivity in fluorine attack at low temperatures.

This process represents the first major advance in direct fluorination since the developments of the "LaMar" technique by Lagow and Margrave[1,2,3] and the "low-temperature, gradient fluorination" techniques by Adcock, Marashin and Lagow.[4,5,6,7,8] The Aerosol process preserves the salient features of the gradient fluorination technique leading to high yields but overcomes two major drawbacks to the gradient process: (a) its batch nature and (b) its reliance on low temperature mass transport to insure maximum surface exposure to elemental fluorine. The need for mass transport at low temperatures unnecessarily slows the fluorination reaction leading to long reaction times.

Experimental Part

Aerosol - Fluorination - System

Results of preliminary experiments

I Test substance: 1,4-dioxane
mp: 11.8°C bp: 101.1°C

Observation of aerosol: optical (Mock assemblies made from "Plexiglas" tubing simulate real conditions and provide for the exclusion of moisture from the system.

A) Parameters for the production of a stable aerosol:

1) Geometry of the generator:

It is necessary, to introduce the chilled helium-nucleating particle flow from the back of the generator, while the hydrocarbon is introduced from below. It is very important, to adjust the relative positions of the two inlet tubes, so that the two streams intersect at natural foci and that neither is directed onto the other's tube. Failure to do this results in poor mixing, the formation of bigger flakes and plugging of the tubes.

2) Nucleating particles:

The chilled helium flow must contain nucleating NaF-particles, which are produced in an oven at 825-875°C. If the temperature of the oven is lower, bigger particles of dioxane (seen as snow-like flakes) are formed. If the oven temperature falls below ∿500°C no aerosol is formed.

3) Temperature of the generator:

It is necessary to keep the generator at a temperature of 30° to 40°C, so that solid hydrocarbon cannot deposit in the generator. This heating is especially important because

the frigid helium flow from the back of the generator and the metal-to-metal contact with the chiller (down to ∿−50°C) tends to cool the generator below 0°C.

It is of advantage to heat the inlet tube for the hydrocarbon-helium carrier flow. This avoids condensation of liquid within the tube and inlet system.

4) Flow-rates for the two flows into the generator:

The variable range for the hydrocarbon-helium flow in the present generator is from 10 to 175 cc/min. For the above flow range the best flow rate for chilled helium-nucleating particle flow is ∿5 dm^3min.

B. Mass Throughputs in the current reactor system:

The mass throughput of dioxane versus the flow-rate of helium through the hydrocarbon reservoir maintained at 34°C is as follows:

flow-rate (cc/min)	mass of hc. (g/h)	flow-rate (cc/min)	mass of hc. (g/h)
18	0.1880	97	0.7596
25	0.2342	112.5	0.9416
42.5	0.2890	130.5	1.0980
58	0.4218	141	1.2090
72.5	0.4926	160	1.3614
75	0.5742	174	1.6206

C. Preliminary Experiments:

All parameters for the production of the aerosol (except flow-rate through the hydrocarbon reservoir) were kept constant at the best values described above.

1) In the first experiments only the chiller-unit was added

to the generator. The chiller was cooled to a temperature between -30 and -50°. The aerosol passed the cooled chiller in a uniform nonturbulent flow for all flow-rates of hydrocarbon.

2) In the second set of experiments the fluorine mixing jet and reactor assembly was added. It was cooled to about the same temperature as the chiller. The aerosol became broader because of the geometry of the reactor. However, it was observed that the aerosol tended to keep away from the cold walls of the reactor. The aerosol was very uniform in optical density.

3) In the third set of experiments a flow of nitrogen was introduced through the fluorine-inlet into the mixing chamber to simulate fluorine-flow into the reactor. It could be easily observed, that the additional flow mixed quite uniformly with the aerosol flow. The only turbulence occurred shortly after starting or stopping this additional flow. The turbulence is probably due to the different densities of the gases. The only problems arose from leaks in the outer cooling system of the reactor at the "O" ring seals. This problem became serious as the reactor temperature was lowered below -40°C. The decision was made to modify the reactor assembly to eliminate the faulty seals.

D. Initial Unsuccessful Fluorination Experiments: 1,4-Dioxane

General Conditions: Optimum parameters described in Part IA were utilized. Specific conditions included chiller (-50° to -55°C), reactor (-50° to -60°C), aerosol trap (-78°C). The

aerosol trap was loosely packed with light copper turnings. Mass throughputs of 1,4-dioxane were determined by comparison of helium flow during the experiment to the calibration graph from data described in IB. Fluorine mole ratios were calculated using an Avogadro's Law-Ideal Gas Law to volume per unit time (flow) relationship.

1) Attempted Complete Fluorination of 1,4-dioxane:

A flow of 1,4-dioxane (0.09 g/h, 1 mmole/hr) was reacted with 150 cc/min helium. On warm up no condensable products were collected. At this point in time the assumption was made that complete combustion to noncondensable products occurred. Two subsequent reactions were run under the same conditions except that the inlet fluorine/helium mixture was precooled with liquid nitrogen. Virtually the same results were obtained. Examination of the interior produced no char or residue. Because of later developments these results are considered inconclusive and suspect. They do not necessarily imply the impracticability of one step complete fluorination.

2) Attempted Monofluorination of 1,4-dioxane:

A flow of 1,4-dioxane (0.74 g/hr, 8.4 mmoles/hr) was reacted with a flow of (4.0 cc/mm, 8 mmoles/hr) fluorine. The major product isolated was unfluorinated dioxane with small amounts of colorless products which from IR and proton NMR appear to be partially fluorinated dioxanes. These materials were difficult to isolate because of their facil decomposition releasing hydrogen fluoride and formation of nonvolatile brown resins or tars. Because of the

difficulties encountered with dioxane, cyclohexane was chosen to replace it as the test substance.

II Test Substance: cyclohexane
mp: 6.5°C bp: 80.7°C

A. Parameters for a stable aerosol:

Because of the similarity of dioxane to cyclohexane the initial experiments are run under conditions similar to the earlier dioxane runs. Optimization experiments later showed that assumption to be essentially correct. It was found, however that the best aerosol was produced when the aerosol generator was operated at 25° to 30°C rather than the 40°C used for the less volatile dioxane. The higher volatility of cyclohexane also results in a finer, more easily vaporized solid aerosol making nucleating particle carrier gas temperatures more critical.

B. Mass throughputs of cyclohexane:

The mass throughput of cyclohexane versus the flow-rate of helium through the hydrocarbon reservoir maintained at 30° to 31°C.

flow-rate (cc/min)	mass of hc. (g/hr)	flow-rate (cc/min)	mass of hc. (g/hr)
16	0.39	42.5	0.85
24	0.525	98.5	2.3
33	0.71	172	4.1

C. Initial Unsuccessful Fluorination of Cyclohexane:

Using reaction parameters similar to those used for dioxane, cyclohexane (.84 g/hr, 10 mmol/hr) was reacted with a flow (4.5 cc/min, 10 mmol/hr) of fluorine diluted with 150 cc/m helium and chilled using liquid nitrogen. On warm up less than 100 mg of

material was collected (1.7g expected). The cause of the problem proved to be back pressure in the system which caused condensation of cyclohexane in the ballast bulb following the hydrocarbon reservoir and in the chiller, leaks accompanying the pressure buildup also resulted in substantial losses. However the product collected proved to be very similar to the product collected in the succeeding runs which were much more successful because of changes made to relieve pressure build up. These changes included elimination of packing in the aerosol trap, enlargement of exit tubing leading to the HF absorbers (NaF pellets) and the product collection traps. The aerosol trap contained only a monel spiral to promote mixing of the aerosol with gaseous fluorine.

D. Successful monofluorination of cyclohexane:

Reaction parameters and conditions similar to those used in part C but with the modifications to reduce back pressure in the system were used. In a two hour run in which cyclohexane (0.84 g/h, 10 mmole/hr) was reacted with fluorine (4.5 cc/mm, 10 mmole/hr) diluted with 150 cc/m helium and chilled with liquid nitrogen, approximately one gram of crude product was collected. The crude product consisted of a mixture of oil and solid. Additional product which was not recovered coated the walls of the reactor and trap and was of low volatility.

Water and hydrogen fluoride was removed by treating the crude product with sodium fluoride and L-4A molecular sieves. A total of 0.880 grams of product was separated by glc giving the following fractions:

Fraction	Product	Amount	Collected
A	Cyclohexane (IR,MS)	170 mg	33%.
B	Monofluoro cyclohexane (IR,MS)[9]	140 mg	27%
C	Mixture, three or four compounds with close retention times, two identified (GCMS) as difluorocyclohexanes.	85 mg	16%
D	Fluorocyclohexane higher than difluoro (IR,MS)	40 mg	12%
E	Fluorocyclohexane higher than difluoro (IR,MS)	20 mg	
F	Mixture of all compounds with retention times longer than 30 minutes at 135°C	65 mg	13%

Additional material of low volatility and low solubility in cyclohexane and carbon tetrachloride has not yet been identified. A small amount of this material becomes nonvolatile upon condensation under vacuum.

Analysis and Discussion of Results of Aerosol Fluorination Experiments.

Although the behavior of dioxane was most advantageous in the development of a stable aerosol generator, the instability of the partially fluorinated species proved to be a severe disadvantage. Because of this instability the dioxane work was discontinued until more is known about the behavior of the aerosol-fluorination system. The data on hand does not convincingly rule out the possibility of perfluorination in a single step. We have discovered since these initial experiments that monofluorination gives a wealth of information on the behavior of the system. For example, the ratio of unfluorinated cyclohexane and more highly fluorinated species to monofluorocyclohexane is a qualitative measure of the efficiency of the reactor design in promoting the uniform mixing of fluorine and the hydrocarbon aerosol, the uniformity of the aerosol and whether all the fluorine

is utilized.

From the data it can be estimated that 33% was unfluorinated, 27% mono fluorianted, 16% difluorinated and 25% was more highly fluorinated. This would indicate that either aerosol nonuniformity or ineffective mixing of fluorine and hydrocarbon, or both, has resulted in nonuniform attack of fluorine on unfluorinated hydrocarbon molecules.

The direction of experiments in progress is to optimize mixing before the ratio of fluorine to hydrocarbon is increased. It is however gratifying to be able to report the successful fluorination of a cyclohexane aerosol in which the system is sufficiently stable to allow the use of product distributions as a measure of the effectiveness of a dynamic process.

List of References

1. J. L. Margrave and R. J. Lagow in Chem. Eng. News, Jan 12, p. 40 (1970).
2. R. J. Lagow and J. L. Margrave, Proc. Natl. Acad. Sci., 67, 4, 8A (1970).
3. R. J. Lagow and J. L. Margrave, J. Polymer Science, 12, 177 (1974).
4. N. J. Maraschin and R. J. Lagow, J. Amer. Chem. Sci., 94, 8601 (1972).
5. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12, 1459 (1973).
6. J. L. Adcock and R. J. Lagow, J. Org. Chem., 38, 3617 (1973).
7. J. L. Adcock and R. J. Lagow, J. Amer. Chem. Soc., 96, 7588 (1974).
8. J. L. Adcock, R. A. Beh and R. J. Lagow, J. Org. Chem., 40, 3271 (1973).
9. M. Rey-Lafon, C. Rouffi, M. Camiade and M. Forel, J. Chim. Phys., 67, 2030 (1970).

APPENDIX

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP 1	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. R. M. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1
Dr. C. Quicksall Georgetown University Department of Chemistry 37th & O Streets Washington, D.C. 20007	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1
Dr. D. B. Brown University of Vermont Department of Chemistry Burlington, Vermont 05401	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1
~~Dr. J. Adcock~~ ~~University of Tennessee~~ ~~Department of Chemistry~~ ~~Knoxville, Tennessee 37916~~	~~1~~
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. M. H. Chisholm Princeton University Department of Chemistry Princeton, New Jersey 08540	1
Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1